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Contact potential difference of alloy steel after heat treatment

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Introduction. The paper considers an actual issue of the development and application of a non-destructive method for controlling the quality of surfaces of steel products (Kelvin probe method). The work objective is to establish the magnitude of the contact potential difference (CPD) of 107WCR5 (KHVG) steel after heat treatment.

Materials and Methods. The object of study is 107WCR5 alloy tool steel. The chemical composition of the samples was refined through the optical emission analysis method. To carry out the statistical processing, there were three samples in three series. We chose different heat treatment modes for each series, i.e., quenching with low tempering, strengthening and normalization. The end surfaces of the samples were polished and then one of them was treated with a solution of nitric acid. Further, the measurement of the contact potential difference and statistical data processing were carried out.

Results. The data obtained show that the CPD value of 107WCR5 steel samples changes after heat treatment. With an increase in tempering temperature, the contact potential difference of the polished surface and the hardness, decrease almost linearly. Exposure to acid causes a significant decrease and equalization of the contact potential difference for all structures. The contact potential difference of steels 107WCR5 and CT105 (U10) is compared. Alloying steel by the elements with the work function values of the electron higher than that of iron causes a decrease in the CPD between the standard and the sample. The CPD behavior under a change in the composition of the steel depends strongly on the presence of alloying elements. The dependence of CPD on the dispersion of the structure is seen in both cases; however, it is more pronounced for 107WCR5 steel. The electron work function of the martensite, troostite, and sorbitol structures obtained as a result of heat treatment of steels 107WCR5 and CT105 is calculated.

Discussion and Conclusions. The dependence of the contact potential difference on the structure, chemical and phase composition was experimentally established; the electron work function of 107WCR5 and CT105 steels was calculated. This technique is more sensitive to alloy steel samples than to carbon steel. It seems possible to conclude that the measurement of the contact potential difference can be used to control surfaces exposed to active media or elevated temperatures as a non-destructive express diagnostic method.

Keywords: contact potential difference, electron work function, alloy steel, heat treatment, Kelvin probe method, nondestructive testing.

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Introduction. The review [1] describes in detail the change in the concept of the electron work function (EWF) and understanding of its nature from the discovery of the photoelectric effect in 1895 by G. Hertz to the consideration on theoretical methods for calculating the EWF. Initially, EWF was defined as the work required to remove an electron from a metal. Over the past hundred years, this fundamental surface property has been measured for virtually all chemical elements and many conductive alloys. Initially, the EWF was measured as the ionization energy, although this is a loose definition since the ionization energy depends on the impurities present on the surface; for a monocrystal, the EWF depends on the orientation of the faces. To date, reliable methods have been developed for

determining the EWF of poly- and monocrystals [2]. One of these methods is the Kelvin probe method, which provides measuring the contact potential difference (CPD) between the surfaces of the reference and the sample under study at the macroscale and to map the CRD at the micro- and nanoscale [3]. Currently, the Kelvin probe method is widely used for nondestructive testing of the surface state and quality [3–7]. For example, in [7], a method was proposed for determining the surface energy of alloys by the magnitude of CPD and hardness, and the EWF values of 30KHGSA, R18, SHKH15 grade steels were obtained.

The contact potential difference is the difference between the electronic work functions of two metal surfaces. The electronic work function (EWF) is defined as the difference between the electrostatic potentials inside the metal φ_i and outside the metal at a certain point φ_0 and the Fermi energy of the metal E_F:

$$\varphi = (\phi_i - \phi_0) - E_F = \Delta\phi - E_F = 4\pi P_S - E_F, \tag{1}$$

where P_S is double layer dipole moment per unit surface area. The dipole moment of the double layer depends on the chemical composition of the surface layers, surface microroughness, adsorbed atoms, presence and density of defects, and crystallographic orientation of the surface. Fermi energy is sensitive to the state of the metal volume, including its chemical composition.

CPD depends on the metal state of the volume and surface, and, therefore, is a structure-sensitive value. The structure and phase composition of steel can be changed through heat treatment.

The work objective was to establish the CPD value for 107WCR5 steel after heat treatment.

Materials and Methods. The study object was alloyed tool 107WCR5 steel. Using the optical emission analysis method, the chemical composition of the samples under study was specified, which has the following average values: 1% C, 1.1% Cr, 1.4% W, 0.95% Mn, 0.25% Si, 0.35% Ni, 0.3% Mo, 0.3% Cu and less than 0.03% sulfur and phosphorus.

For the reliability of experimental data and statistical processing, the number of samples in the series was 3 units. To establish the effect of heat treatment modes on the CPD, three different modes were selected: quenching with low tempering, improvement, and normalization. The quenching temperature of the first and second series of samples was 820° C. Mineral oil was used as a cooling medium, which provided a cooling rate higher than the critical one in accordance with the diagram of the decomposition of austenite for 107WCR5 steel. Next, for the first group of samples, a low tempering was carried out at a temperature of 180° C, and additional self-cooling. For the second group of samples, tempering at temperatures of 600° C and 400° C was performed. For the third group, normalization by heating to 820° C and air cooling were carried out. The opposite ends of the samples corresponded to different preparation technologies: side A was ground after heat treatment, side B, in addition to grinding, was etched with 4% nitric acid solution in ethyl alcohol.

Hardness of the samples was measured by the Rockwell method to control the resulting structures after heat treatment.

The CPD was measured by the Kelvin probe method on a laboratory bench developed at the Research and Educational Center “Materials”, DSTU (Fig. 1)[1]. The reference electrode, taken as a standard, was made of stainless 12X18H10T steel, it was not subjected to any external actions (radiation, effect of strong electric and magnetic fields, heating and cooling, interaction with chemical reagents, etc.) and was used in all measurements. The sample was fixed on a metal table using a clamp (Fig. 1). The surface was located strictly parallel to the reference electrode. Electrical contact was provided between the clamp, the sample and the metal table.

[1] Sukiyazov AG, Zelentsov VB, Aizikovich SM, et al. Bench for measuring electronic work function from the surface of metal bodies. RF Patent 177 659, 2018. (In Russ.)

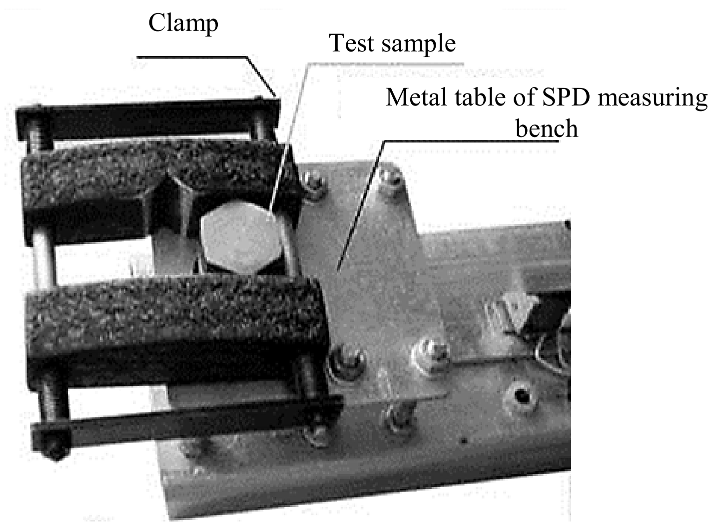


Fig. 1. Sample of 107WCR5 steel located on a metal table of measuring bench

Research Results. The CPD measurement results have good reproducibility. Statistical processing was carried out according to the Student's test method. The data obtained show that the CPD value of the samples from 12X18H10T steel changes after heat treatment (Fig. 2). As a result of normalization, a sorbitol structure (with an intermellar distance of ~ 0.4–0.2 μm) with hardness of 22 HRC, which had the minimum CPD values and hardness, was obtained. The highest CPD and hardness values are observed in the tempered martensite structure with carbides obtained as a result of quenching and low tempering at 180° C [8–10]. With an increase in the tempering temperature, the CPD value of the polished surface, as well as hardness, decreases almost linearly (Fig. 2). After processing the surface of 12X18H10T steel with a 4% solution of nitric acid, a film consisting of iron, chromium and tungsten nitrates is formed according to the ion exchange reaction. The acid action causes a significant decrease in the average CPD value for all the structures obtained, that is, the CPD values become approximately the same (Fig. 2).

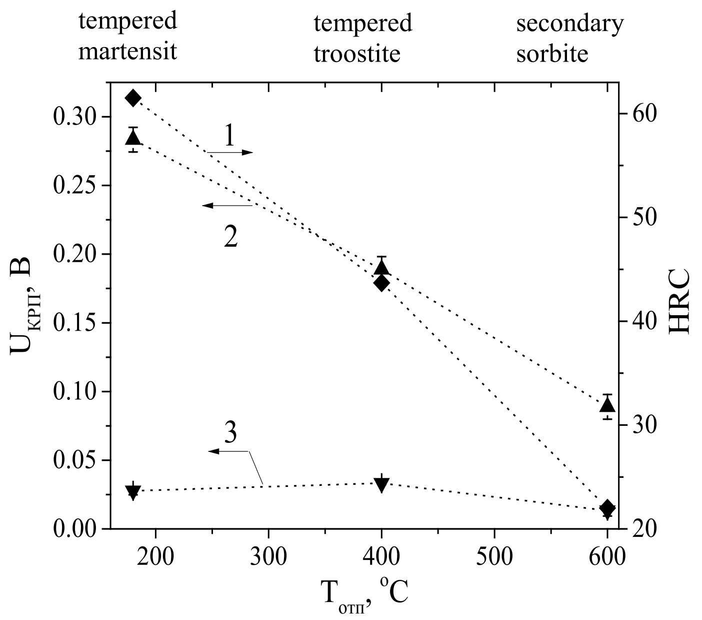
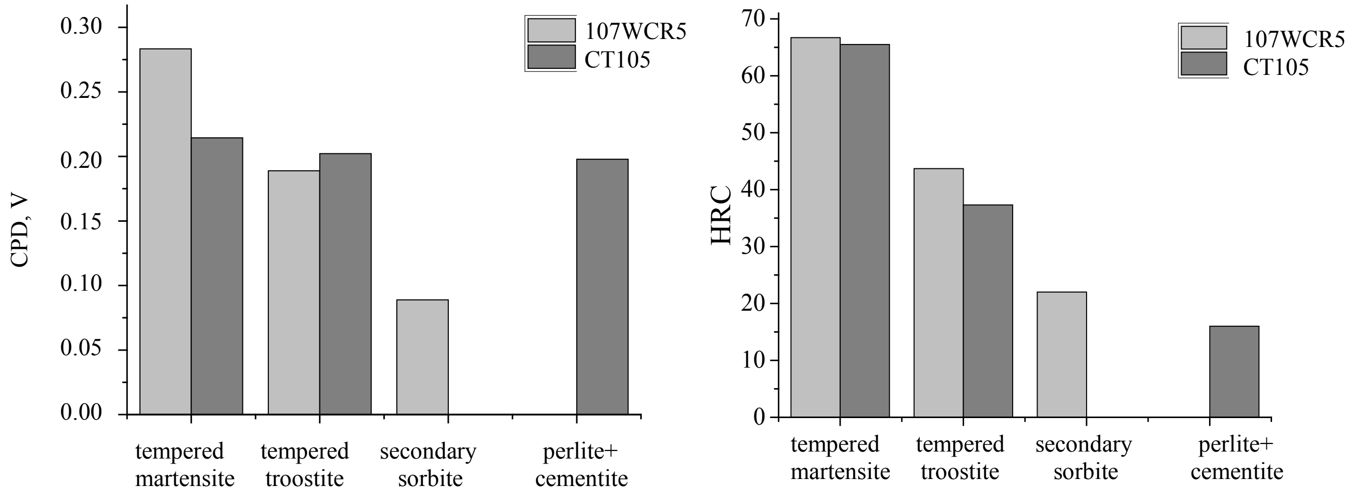


Fig. 2. Effect of tempering temperature on the contact potential difference of 107WCR5 steel: 1 — hardness, 2 — CPD of the polished surface, 3— CPD of the surface after etching

As is known, alloying elements change not only the critical temperatures of phase transformations, but also most of the steel properties [11–13]. For example, the material hardness increases. In this regard, it is advisable to analyze the influence of alloying on the steel CPD, that is, on the value of the electronic work function. The CPD data of 12X18H10T steel were compared to the results of measuring the CPD of U10 carbon tool steel with the same carbon content and a similar structural condition. Alloying steel with elements having higher electronic work function than iron causes a decrease in the CPD between the standard and the sample (Fig. 3). An exception is the structure of tempered martensite, in which there is an increase (by 0.06 V) in the CPD value, in comparison with CT105 steel tempered martensite CPD. Furthermore, different structures of alloy steel have sharper differences in the CPD values than in the

case of carbon steel. The CPD behavior when changing the steel composition strongly depends on the presence of alloying elements. The CPD dependence on the fineness of the structure is visible in both cases, however, for 12X18H10T steel, it is more pronounced.



a) *b)*

Fig. 3. Histograms of CPD values (*a*) and HRC hardness (b) for 107WCR5 and CT105 steels

According to the reference data [14], the electronic work function in stainless 12Kh18N10T steel was taken to be 3.67 eV. Based on the definition of the physical CPD value as the difference between the work functions of two parallel surfaces of different metals that form a capacitor, it is possible to write an expression for the electronic work function of the test sample in the form:

$$\varphi = \varphi_{эт} - eU_{КРП} . \quad (2)$$

According to the expression (2), the EWF value of the structures of martensite, troostite and sorbite obtained under the heat treatment of 107WCR5 and CT105 steels was estimated (Fig. 4). Since the CPD values for all investigated structures are positive, the EWF of these structures is less than the EWF of the reference sample. The dependences of the EWF value of the samples under study on the structure differ significantly. For CT105 steel, the change in the EWF value does not exceed hundredths of eV, while for 107WCR5 steel, the difference in the EWF value of sorbite and troostite structures reaches 0.1 eV, i.e., it makes up 3% of the EWF value of troostite. The EWF of tempered martensite with carbides of 107WCR5 steel is 3.45 eV. Thus, we can conclude that the following factors influence the EWF value: phase composition (different structural condition obtained under different heat treatment modes), chemical condition (dissolution of elements or formation of chemical compounds on the sample surface) and structure dispersion. Dispersion is regarded as the difference in the sizes of the plates of the tempered products (perlite, sorbite, troostite). For alloy steel, the difference between tempered structures affects significantly the EWF value (Fig. 4). At the same time, for CT105 steel, this difference is almost invisible in Fig. 4.

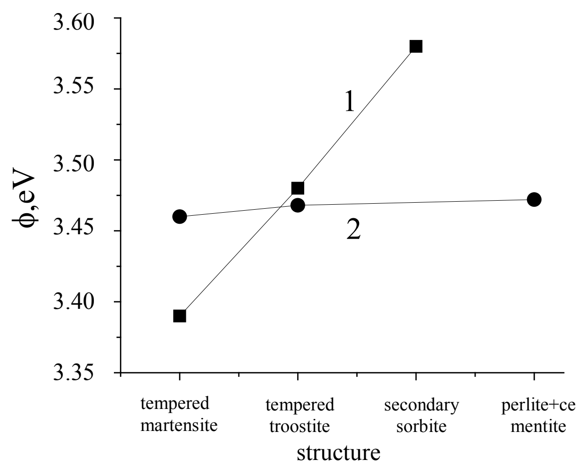


Fig. 4. Dependence of the EWF on the phase composition of steel: 1 — 107WCR5 steel; 2 —CT105 steel

Discussion and Conclusions. The dependences obtained show the correlation between the change in hardness and the CPD value. Since the CPD of all samples is positive, their EWF is less than the EWF of the standard used. The structure of tempered martensite has the highest CPD value. It is found that the CPD decreases with an increase in the tempering temperature. The addition of alloying elements with higher EWF values causes a decrease in the CPD between the studied samples with the structures of ferrite-cementite mixtures, secondary carbides, and the standard. Alloying elements increase considerably the CPD value variation under changing the structural condition of the alloy in comparison with carbon steel. The dependence of the CPD value on the structure, chemical and phase composition of steels is experimentally established. The EWF value of CT105 and 107WCR5 steels was estimated. It can be seen from the results obtained that this method is more sensitive to alloy steel samples than to carbon steel. Thus, we can conclude that the measurement of the CPD can be used as a non-destructive diagnostic express-method under monitoring surfaces exposed to active media or elevated temperatures.

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Claimed contributorship

L. P. Aref'eva: basic concept formulation; research objectives and tasks setting; computational analysis and analysis of the research results; text preparation; formulation of conclusions. A. G. Sukiyazov: academic advising; testing; analysis of the research results; the text revision; correction of the conclusions. Yu. V. Dolgachev: analysis of the test results; text preparation; correction of the conclusions. L. S. Shakhova: sample preparation and testing; the text revision; text layout and graphical presentation of the research results.

All authors have read and approved the final manuscript.